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(58) Field of search
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(71) Applicants
Toyo Engineering
Corporation, No. 2—5,
Kasumigaseki 3-chome,
Chiyoda-ku, Tokyo, Japan
(72) Inventors
Keizo Konoki,
Takanobu Shinohara,
Keiichi Shibata
(74) Agents
Graham Watt & Co.,
Riverhead, Sevenoaks,
Kent TN13 2BN

(54) **Apparatus for high-
temperature treatment of
hydrocarbon-containing materials**

(57) In the treatment of a hydrocarbon-containing material at temperatures of 500°C or above in apparatus made of a nickel-containing heat-resistant steel, the surfaces of the apparatus that are exposed to the hydrocarbon-containing material are coated with nickel-free materials consisting of metals selected from titanium, cobalt, chromium, iron or alloys thereof (optionally containing aluminium or aluminium and silicon),

nickel-free steels (optionally containing aluminium or aluminium and silicon), silicon nitride or carbide, boron nitride or refractory oxides selected from alumina, silica, titania and chromia. The coating decreases the rate of deposition of carbon on the coated surface, and acts as a carburization barrier minimizing ingress of carbon into the nickel steel and resultant embrittlement. Treatment processes involving the protected apparatus include steam reforming, thermal cracking and partial oxidation and the steam cracking of ethane is particularly described.

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SPECIFICATION

High-temperature treatment of hydrocarbon-containing materials

The present invention relates to high-temperature treatment of hydrocarbon-containing materials. More particularly, this invention relates to processes wherein a hydrocarbon, a mixture of a hydrocarbon
 5 and steam and/or an oxygen-containing gas, or a mixture of a hydrocarbon and one or more of the following gases, namely hydrogen, carbon monoxide and carbon dioxide, is subjected to a chemical reaction, such as thermal cracking, steam reforming, partial oxidation, or to some other high-temperature treatment. Such materials to be treated will hereinafter be referred to simply as "hydrocarbon-containing materials".

10 Nowadays, ethylene, hydrogen, or a mixture of hydrogen and carbon oxides, are produced on a large scale by subjecting a hydrocarbon-containing material to thermal cracking, steam reforming and/or partial oxidation at high temperature and high pressure in the presence or absence of a catalyst. Before or after and during such chemical reactions, the hydrocarbon-containing material is exposed to high temperature. Thus, its hydrocarbon component undergoes thermal decomposition, which results in
 15 a deposition of solid carbon. Since this solid carbon tends to accumulate on the surfaces of the reactor and other apparatus that are exposed to the hot gaseous hydrocarbon-containing material, it is necessary to shut down the production plant periodically to remove the deposited carbon for keeping its accumulation within bounds.

20 Apparatus for handling a hydrocarbon-containing material at high temperature commonly makes use of nickel-containing steels which can retain adequate strength even under the high-temperature process conditions. Carburization of such steels can, however, lead to their embrittlement. We have found that the deposition of solid carbon is promoted by catalytic action of the nickel contained in these steels.

25 Our present invention aims to reduce substantially or to eliminate carbon deposition in high temperature treatments of hydrocarbon-containing materials. We also aim to provide a process for the high-temperature treatment of a hydrocarbon-containing material in which apparatus made of a nickel-containing metal and used for handling the hydrocarbon-containing material at high temperature can be prevented from becoming brittle owing to the occurrence of carburization.

30 According to the present invention, there is provided a process for treating a hydrocarbon-containing material at temperatures of 500°C or above in an apparatus made of a nickel-containing heat-resistant steel, the hydrocarbon-containing material consisting of a hydrocarbon, a mixture of a hydrocarbon and steam and/or an oxygen-containing gas, or a mixture of a hydrocarbon and one or more of the following gases, namely hydrogen, carbon monoxide, carbon dioxide and olefins. characterised by conducting the treatment in apparatus the surfaces of which exposed to the
 35 hydrocarbon-containing material are coated with

- (a) material selected from titanium, cobalt, chromium, iron and alloys thereof;
- (b) material selected from titanium, cobalt, chromium, iron and alloys thereof containing aluminium or aluminium and silicon;
- (c) a nickel-free steel;
- 40 (d) a nickel-free alloy steel containing aluminium or aluminium and silicon;
- (e) material selected from alloys of titanium and niobium and alloys of copper and chromium; or
- (f) material selected from alumina, titania, silica, silicon carbide, silicon nitride, boron nitride and chromia.

The invention also provides a process for reacting a hydrocarbon with steam and/or an oxygen-containing gas at high pressure in a reactor made of a nickel-containing heat-resistant steel to produce
 45 a gaseous mixture containing hydrogen and carbon monoxide, the improvement which comprises conducting the reaction in a reactor the surfaces of which exposed to the hydrocarbon are coated with

- (a) material selected from titanium, cobalt, chromium, iron and alloys thereof;
- (b) material selected from titanium, cobalt, chromium, iron and alloys thereof containing aluminium or aluminium and silicon;
- 50 (c) a nickel-free steel;
- (d) a nickel-free alloy steel containing aluminium or aluminium and silicon;
- (e) material selected from alloys of titanium and niobium and alloys of copper and chromium; or
- (f) material selected from alumina, titania, silica, silicon carbide, silicon nitride, boron nitride and chromia.

55 The invention further provides apparatus for use in a process wherein a hydrocarbon-containing material is treated at temperatures of 500°C or above, said apparatus or components thereof being made from nickel-containing heat-resistant alloy, and surfaces of the apparatus or components which are exposed to the hydrocarbon-containing material are coated with:

- (a) material selected from titanium, cobalt, chromium, iron and alloys thereof;
- 60 (b) material selected from titanium, cobalt, chromium, iron and alloys thereof containing aluminium or aluminium and silicon;
- (c) nickel-free steel;
- (d) a nickel-free alloy steel containing aluminium or aluminium and silicon;
- (e) material selected from alloys of titanium and niobium and alloys of copper and chromium; or

(f) material selected from alumina, titania, silica, silicon carbide, silicon nitride, boron nitride and chromia.

The invention is now described hereunder in more detail by way of example only.

In the practice of the present invention, any of the coating materials belonging to the aforesaid categories (a) to (f) may be used to coat those surfaces of the apparatus that are exposed to the hydrocarbon-containing material to be treated. These coating materials are more specifically explained in the following. 5

Among the metallic materials belonging to the category (a), typical examples of the alloys of iron and chromium are an iron-chromium alloy containing 17 to 19% by weight of chromium and 0.3% by weight of carbon, and an iron-chromium alloy containing 26 to 28% by weight of chromium and 0.1% by weight of carbon. In each of these alloys, and in the examples following unless stated otherwise, the balance ignoring impurities is the first-mentioned metal. 10

Typical examples of the alloys belonging to the category (b) are a titanium-aluminium alloy containing 6% by weight of aluminium and a Ti-Al-Zr-V alloy containing 6% by weight of aluminium, 4% by weight of zirconium, and 1% by weight of vanadium. 15

A typical example of the alloys belonging to the category (d) is an Fe-Cr-Al-Si alloy containing 23% by weight of chromium, 1.5% by weight of aluminium, and 1.5% by weight of silicon.

The alloys of titanium and niobium belonging to the category (e) may consist of 91 to 99% by weight of titanium 1 to 3% by weight of niobium and 0 to 2% by weight each of the other components such as zirconium, aluminium and tantalum. The alloys of copper and chromium belonging to the category (e) may consist of 95 to 99% by weight of copper, 1 to 3% by weight of chromium, and 0 to 2% by weight of other components such as beryllium. 20

No particular limitation is placed on the method by which the surfaces of the apparatus that are exposed to the hydrocarbon-containing material are coated with a metallic material belonging to any of the aforesaid categories (a) to (e). However, this coating is usually accomplished by the so-called casting method in which a melt of the metallic coating material is poured over the apparatus components to be covered, the components having previously been formed into tubes, plates or other members. For producing high temperatures, such means as acetylene burners and electric arcs can be used instead to cause a melt of the metallic material to adhere to the surfaces to be covered. In another method, a melt of the metallic material is sprayed and deposited on the surfaces to be covered, for example by the flame spraying or plasma jet processes. A chemical vapour deposition method could be used in which the metallic compound is vaporized, contacted with the surfaces to be coated and subjected to a chemical reaction thereon. A physical vapour deposition method could also be used, e.g. involving ionizing one or more metals or an alloy in a high vacuum. The resulting ions are then supplied with kinetic energy in an electric field and led into a plasma or other space where they are directly deposited on the surfaces to be coated or are subjected to a chemical reaction to deposit the metal thereon. A further method is the so-called cladding method in which tubes, plates or other members are separately fabricated from the metallic (cladding) material and are bonded to the surfaces of the previously-shaped components by the application of pressure. 25 30 35

When the nickel-containing structural components are coated with a metallic material belonging to any of the aforesaid categories (a) to (e) and are used at high temperature, a slight degree of interdiffusion or mixing of components occurs between the nickel-containing structural material and the coating material. It is desirable, therefore, that the coating material has a thickness of not less than 100 microns in the interests of long-term service. The shaped and coated structural components may further be subjected to bending, tube-expanding, welding and other working operations to fabricate therefrom an apparatus or its parts having any desired shapes. However, if the coated structural components are in the form of castings, it is desirable not to subject them to bending, tube-expanding, or other working operations. 40 45

The method of coating the structural components with non-metallic materials belonging to the aforesaid category (f) depends on the type of the non-metallic material. 50

(A) If the non-metallic material is an oxide, coating can be accomplished by the so-called spraying method in which the oxide is melted and sprayed on the surfaces to be coated such as by the flame spraying or the plasma jet process. The so-called baking method could be used instead, in which a suspension of the oxide is applied to the surfaces to be coated followed by baking at high temperature. In the latter case, however, it is desirable to bake the oxide in combination with a mixture consisting of varying proportions of oxides selected from silica, alumina, boron oxide, calcium oxide, zinc oxide, barium oxide, zirconium oxide and the like, for the purpose of reducing the melting temperature of the oxide to lower than that of the structural material and thereby preventing melting or alteration of the structural material. The service temperature of the coated component obtained by this baking method is limited to the melting temperature of the covering layer. 55 60

(B) If the non-metallic material is silicon carbide, silicon nitride or boron nitride, the coating can be accomplished by the method in which a melt or solution of a compound containing silicon-to-carbon, nitrogen-to-boron or nitrogen-to-silicon bonds is applied to the surfaces to be coated of the structural material and then subjected to a chemical reaction in air or an inert gas at high temperature to deposit the desired compound thereon. The above-described spraying method may be used, in which a powder 65

or rod of silicon carbide, boron nitride or silicon nitride is melted and sprayed on the surfaces to be coated according to the plasma jet process. The above described chemical or physical vapour deposition methods could also be chosen.

Where the surfaces are to be coated with material in the aforesaid category (f), the structural components may once again be tubes, plates or any other members. When such a non-metallic material is used, a coating layer having a thickness of not less than 10 microns is generally required. However, the thickness of the coating layer is desirably not greater than 1 millimeter. This is because, when an apparatus having an unduly thick coating layer is subjected to or participates in a heating step, the coating layer not only reduces the overall coefficient of heat transfer to interfere with the flow of heat therethrough, but also is liable to spall off owing to the difference in thermal expansion coefficient between the structural component and the coating material.

Among nickel-containing components coated with the above-described coating materials, tubes are particularly important because they are often used inter alia as reactors and heat exchangers, and, therefore, have abundant opportunities of being contacted by hot hydrocarbon-containing materials. Accordingly, depending on the pathway by which a hydrocarbon-containing material flows through a reactor or heat exchanger, it may often be necessary to coat not only one surface of the tube but both surfaces thereof.

No particular limitation is placed on the hydrocarbon to be treated. Specific examples range from hydrocarbons having a small number of carbon atoms, such as methane, ethane, etc., to hydrocarbons having a large number of carbon atoms, such as heavy oil obtained as a distillate by subjecting reduced crude to vacuum distillation. Generally speaking, the hydrocarbon which is treated in the practice of the present invention has an H/C atomic ratio of 2.0 to 4.0. The present invention is significantly effective when it is applied to the treatment of the aforesaid heavy oil.

The above-described hydrocarbon may be used alone in the form of a gas or liquid. Alternatively, it may be used in admixture with steam and/or an oxygen-containing gas, or in admixture with hydrogen, carbon monoxide, carbon dioxide and/or olefins (they may represent a product gas obtained by treating a hydrocarbon or a mixture of a hydrocarbon and steam and/or an oxygen-containing gas). The hydrocarbon content in such mixtures is usually in the range of 10 to 60% by weight.

The term "treat" as used herein means not only to subject a hydrocarbon-containing material to a chemical reaction such as thermal cracking, steam reforming and partial oxidation, but also to handle a feed stream and a product stream before and after this chemical reaction.

In the practice of the present invention, the hydrocarbon-containing material is treated at temperatures of 500°C or above. Moreover, this treatment is preferably carried out at a pressure of 6 to 100 kg/cm²G. Apparatus for treatment under such severe conditions is ordinarily constructed from nickel-containing materials such as nickel-containing heat-resistant steels.

In accordance with one feature of the present invention, when a hydrocarbon-containing material is treated at temperatures of 500°C or above and especially when it is subjected to a chemical reaction, such as thermal cracking, steam reforming or partial oxidation, in the presence or absence of a catalyst, the deposition and accumulation of solid carbon on the surfaces of the reactor that are exposed to the hydrocarbon-containing material can be decreased significantly. If the deposited and accumulated solid carbon is left to accumulate, it interferes with the passage of a fluid containing the hydrocarbon and causes an increase in pressure loss. Moreover, in cases where it is necessary to remove or supply the heat of reaction for the purpose of effecting the chemical reaction, the accumulated solid carbon also causes a marked decrease in overall coefficient of heat transfer and thus makes it difficult to continue the operation. As a counter-measure, therefore, it is necessary to shut down the system at regular intervals and remove the deposited carbon by any of the well-known techniques. By adopting the present invention, the frequency of this carbon-removing operation can be reduced to 2/3 less of that required hitherto.

Another feature of the present invention is that the carburization of the nickel-containing structural material can be diminished greatly. It is well known that, when a carbon steel or an alloy steel containing nickel and chromium, and the like are exposed to carbon-containing substances, such as hydrocarbons, carbon oxides, etc., at temperatures of 700°C or above, the so-called carburization phenomenon occurs. That is, their carbon component infiltrates and diffuses into the microstructure of the steel and thereby reduces its strength to such a degree that the steel is no longer fit for use. It is said that such carburization is not only due to the infiltration and diffusion of the deposited carbon into the microstructure of the steel but also attributable to the presence of a gaseous carbon-containing substance. The present invention makes it possible to prolong the service lives of components, such as reactor tubes and ducts, which would otherwise have to be replaced at intervals of 2 or 3 years, by providing an effective carbon barrier.

The present invention can produce marked effects when it is applied to components or apparatus made of a nickel-containing heat-resistant steel and used at temperatures of 500°C or above and specifically to the surfaces thereof that are exposed to a stream of hydrocarbon-containing material. Although these may have any desired shapes, tubular members used as reactors are particularly important. This is because, in the reactor, the stream of hydrocarbon-containing material usually reaches a maximum temperature, the deposition of carbon is most likely to occur owing to the necessity

of removing or supplying a large amount of reaction heat, and the reduction in overall coefficient of heat transfer caused by the deposited carbon leads to the greatest trouble.

The present invention is further illustrated by the following non-limiting examples.

EXAMPLE

- 5 Ethane was subjected to steam cracking in reactor tubes having an inner diameter of 27 mm and a length of 800 mm. These reactor tubes were made of a nickel-containing alloy steel (Fe-20% Ni-25% other alloying elements) and had their inner surfaces covered with the respective covering materials shown in Table 1. The ratio of ethane to steam was 7 : 3 and the reactor tube was maintained at a temperature of 700°C or 1,100°C by external heating. After the operation had continued for 10 hours at a pressure of 1 kg/cm²G and at a feed rate of 100 cc/min, the conditions of carbon deposition on the inside surface of the reactor tube was examined. The results thus obtained are summarized in Table 1.

TABLE 1

Coating Material on Inside Surface of Reactor Tube
and Conditions of Carbon Deposition

Test Tube No.	Coating Material on Inside Surface of Tube	Testing Temperature (°C)	Conditions of Carbon Deposition on Inside Surface of Tube	
			Amount Deposited (mg / cm ² / 10 hr)	Form
1	Chromium	1,000	1.0	Filmy
2	Fe-28%Cr Alloy	1,000	2.1	Filmy
3	Ti-6%Al Alloy	700	0.3	Sootlike
4	Fe-23%Cr-1.5%Al-1.5%Si Alloy	1,000	2.1	Filmy
5	Ti-2%Nb Alloy	700	0.3	Sootlike
6	Cu-1%Cr Alloy	700	<0.1	Sootlike
7	Alumina	1,000	2.0	Filmy
8	Titania	1,000	1.4	Filmy
9	Silica	1,000	1.6	Filmy
10	Silicon Carbide	1,000	1.2	Filmy
11	Silicon Nitride	1,000	1.4	Filmy
12	Boron Nitride	1,000	1.4	Filmy
13	Chromia	1,000	1.0	Filmy
14	None	1,000	3.4	Filmy

- As is evident from the data shown in Table 1, a considerable degree of carbon deposition was noted on the uncovered inside surface of a tube made of a nickel-containing steel, even in the case of steam cracking of ethane which is a light hydrocarbon. This carbon deposition was decreased to a substantial degree by coating that surface with a nickel-free metallic or non-metallic material. Among others, chromium, a titanium-niobium alloy and a copper-chromium alloy were found to be particularly excellent coating materials.

CLAIMS

1. A process for treating a hydrocarbon-containing material at temperatures of 500°C or above in an apparatus made of a nickel-containing heat-resistant steel, the hydrocarbon-containing material consisting of a hydrocarbon, a mixture of a hydrocarbon and steam and/or an oxygen-containing gas, or a mixture of a hydrocarbon and one or more of the following gases, namely hydrogen, carbon monoxide, carbon dioxide and olefins, characterised by conducting the treatment in apparatus the surfaces of which exposed to the hydrocarbon-containing material are coated with
 - (a) material selected from titanium, cobalt, chromium, iron and alloys thereof;
 - (b) material selected from titanium, cobalt, chromium, iron and alloys thereof containing aluminium or aluminium and silicon;
 - (c) a nickel-free steel;
 - (d) a nickel-free alloy steel containing aluminium or aluminium and silicon;
 - (e) material selected from alloys of titanium and niobium and alloys of copper and chromium; or
 - (f) material selected from alumina, titania, silica, silicon carbide, silicon nitride, boron nitride and chromia.
2. A process for reacting a hydrocarbon with steam and/or an oxygen-containing gas at high pressure in a reactor made of a nickel-containing heat-resistant steel to produce a gaseous mixture containing hydrogen and carbon monoxide, the improvement which comprises conducting the reaction in a reactor the surfaces of which exposed to the hydrocarbon are coated with
 - (a) material selected from titanium, cobalt, chromium, iron and alloys thereof;
 - (b) material selected from titanium, cobalt, chromium, iron and alloys thereof containing aluminium or aluminium and silicon;
 - (c) a nickel-free steel;
 - (d) a nickel-free alloy steel containing aluminium or aluminium and silicon;
 - (e) material selected from alloys of titanium and niobium and alloys of copper and chromium; or
 - (f) material selected from alumina, titania, silica, silicon carbide, silicon nitride, boron nitride and chromia.
3. A process as claimed in claim 1 or claim 2 wherein the surfaces that are exposed to the hydrocarbon are coated with chromium, a titanium-niobium alloy or a copper-chromium alloy.
4. A process according to claim 1 or claim 2 and substantially as herein described by way of example.
5. Apparatus for use in a process wherein a hydrocarbon-containing material is treated at temperatures of 500°C or above, said apparatus or components thereof being made from nickel-containing heat-resistant alloy, and surfaces of the apparatus or components which are exposed to the hydrocarbon-containing material are coated with:
 - (a) material selected from titanium, cobalt, chromium, iron and alloys thereof;
 - (b) material selected from titanium, cobalt, chromium, iron and alloys thereof containing aluminium or aluminium and silicon;
 - (c) a nickel-free steel;
 - (d) a nickel-free alloy steel containing aluminium or aluminium and silicon;
 - (e) material selected from alloys of titanium and niobium and alloys of copper and chromium; or
 - (f) material selected from alumina, titania, silica, silicon carbide, silicon nitride, boron nitride and chromia.
6. Apparatus according to claim 5, wherein the surfaces that are exposed to the hydrocarbon are coated with chromium, a titanium-niobium alloy or a copper-chromium alloy.
7. Apparatus according to claim 5, wherein the said surfaces are coated with an Fe-Cr alloy containing 17 to 19% Cr and 0.3% C by weight or an Fe-Cr alloy containing 26 to 28% Cr and 0.1% C by weight.
8. Apparatus according to claim 5, wherein the said surfaces are coated with a Ti-6% by weight Al alloy or a Ti-Al, 4% Zr and 1% V alloy, the latter percentages being by weight.
9. Apparatus according to claim 5, wherein the said surfaces are coated with an Fe-23% Cr, 1.5% Al and 1.5% Si alloy, the percentages being by weight.
10. Apparatus according to claim 5, wherein the said surfaces are coated with an alloy consisting of 91 to 99% Ti, 1 to 3% Nb and 0 to 2% of one or more of the metals Zr, Al and Ta, the percentages being by weight.
11. Apparatus according to claim 5, wherein the said surfaces are coated with alloy consisting of 95—99% Cu, 1 to 3% Cr and 0 to 2% of other components.
12. Apparatus according to claim 5 and substantially as herein described by way of example.